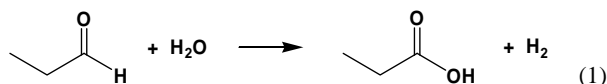# Aldehyde-Water Shift Catalysis: $H_2$ Production from Water and Aldehydes via a Homogenous Dirhodium Tetraphosphine Catalyst

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## Introduction

A new catalytic reaction to produce $H_2$ from aldehydes and water has been discovered (eq. 1).



$$\text{(1)}$$

This is called aldehyde-water shift catalysis in analogy with the water-gas shift reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$. The aldehyde-water shift reaction is thermodynamically downhill with $\Delta G° (363K) = -28.4$ kJ/mol, $\Delta H° = -9.6$ kJ/mol, and $\Delta S° = 51.9$ J/molK. The proposed catalyst for this reaction is $[rac\text{-}Rh_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)](BF_4)_2$, **1**, shown below.
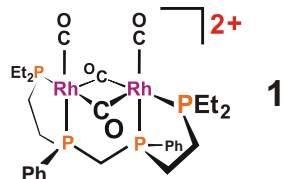


The potential of this catalysis for fuel cell applications comes from the possibility of using formaldehyde to make formic acid and $H_2$, followed by decomposition of the formic acid to make another $H_2$ and $CO_2$ (eq. 2):



$$\text{(2)}$$
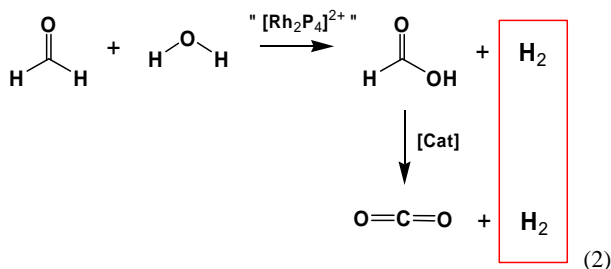
A formaldehyde-water mixture has one of the highest $H_2$ energy storage capacities on a per weight basis for fuel cell applications.

## Experimental

The catalyst precursor used was $[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$ (nbd = norbornadiene) prepared according to literature methods,[1] or $[rac\text{-}Rh_2(CO)_4(et,ph\text{-}P4)](BF_4)_2$ prepared and isolated from the carbonylation of the norbornadiene complex (details available from the principle author). 1-hexene, heptaldehyde, acetaldehyde, and acetone were all obtained from Aldrich and degassed with $N_2$ prior to use. 1-hexene was further purified by passing it through a short alumina column under $N_2$ prior to use. This removes any peroxide impurities that can deactivate the dirhodium catalyst. Water was normal distilled water from our in-house system and also degassed with $N_2$ prior to use.

Catalytic reactions were performed in 150 mL Parr 4560 mini-reactors equipped with standard thermocouples, pressure transducers and Parr packless magnetic stirrers. Data was collected and partially analyzed on Parr 4850 or 4870 process controllers. The autoclave is configured to run under constant pressure with gas being supplied from a 1 L high pressure reservoir equipped with a pressure transducer and dual stage regulator. The autoclave set-up is shown in Figure 1. Products were analyzed on HP 5890 GC using a DB-1 30m capillary column or on a HP GC-MS system.
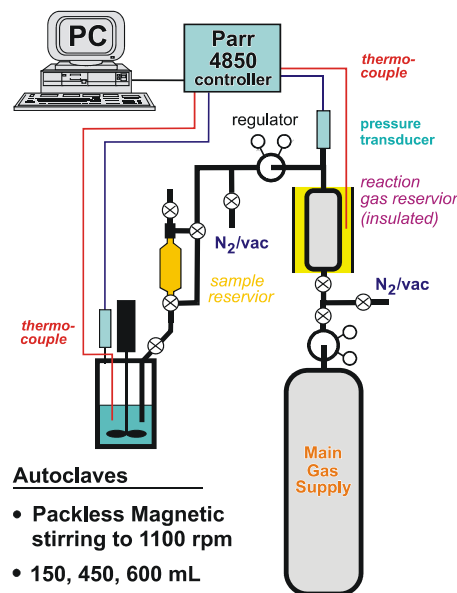


**Figure 1.** Schematic of autoclave setup.

**Tandem Hydroformylation and Aldehyde-Water Shift Catalysis.** With our current batch autoclave setup the most consistent results are obtained by first starting the catalysis under hydroformylation conditions using 1-hexene as the starting substrate and a 1:1 mixture of $H_2/CO$ gas. The autoclave was loaded under an inert atmosphere with 1.0 mM $[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$ and 80 mL of 30% water (by volume) in acetone. The autoclave was then purged three times with $H_2/CO$, and the catalyst solution stirred at 1000 rpm stirring for 15-20 min under 45 psig 1:1 $H_2/CO$ as the temperature was increased to 90ºC. After the temperature has stabilized at 90ºC the pressure of the reaction vessel was decreased to ~45 psig and 1000 equivalents of 1-hexene (99+% and passed through a neutral alumina column under inert atmosphere immediately prior to use, $8.9 \times 10^{-2}$ mol, 11 mL) was pushed into the autoclave with 90 psig of $H_2/CO$. The progress of the reaction was monitored by gas uptake from a higher pressure gas storage reservoir connected to a two-stage regulator delivering synthesis gas at a constant pressure of 90 psig to the reaction vessel.

After 10 min of hydroformylation (representing approximately 80% conversion of the 1-hexene to heptaldehyde) the gas supply to the autoclave is turned off and the $H_2/CO$ gas in the high pressure reservoir is replaced with pure CO. This takes about 5 mins. The autoclave is then opened to the pure CO reservoir. Aldehyde-water shift catalysis occurs during this period converting the heptaldehyde to heptanoic acid and $H_2$. The rapid build-up of $H_2$ in the autoclave typically stops the aldehyde-water shift catalysis at about 75-80% conversion of the aldehyde to carboxylic acid.

**Simple Flow-Reactor Studies.** Aldehyde can be directly reacted with water to make carboxylic acid and $H_2$ using a simple flow setup in our autoclaves. After the initial catalyst precursor ($[rac\text{-}Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$) soaks under 1:1 $H_2/CO$ at 90 ºC to generate the active catalyst, the feed gas is switched to 90 psig of pure CO and a needle valve is employed to constantly purge the

reaction vessel. 1000 equivalents of heptaldehyde are pressure added to the catalyst solution and a CO purge rate of 4-5 psig/min (based on the pressure drop in the high pressure reservoir cylinder) provided good conditions for aldehyde-water shift catalysis. A maximum of about 75% conversion to carboxylic acid was achieved, with an approximate turnover frequency of 1000 TO/hr (from GC analysis) and with undetectable side products. The aldehyde-water shift catalysis is quite sensitive to reaction conditions and both timing and proper purge rates are critical to achieve good conversion. These are still being optimized.

**Results and Discussion**

The most consistent results for the aldehyde-water shift catalysis have been obtained by first performing hydroformylation catalysis on 1000 equivalents (1M concentration) of 1-hexene (smaller 1-alkenes are expected to work fine for this as well) under our standard reaction conditions: 90ºC, 90 psig 1:1 $H_2/CO$, and 30% water (by volume) and acetone as the solvent.[2] Water-acetone solvent dramatically stabilizes our highly active and selective dirhodium catalyst system by inhibiting fragmentation to unreactive species.[2] After 10 mins of rapid hydroformylation, approximately 80% of the 1-hexene has been converted to heptaldehyde. At this point the $H_2/CO$ gas feed to the autoclave is turned off and then switched over to pure CO. The continuing hydroformylation rapidly generates $H_2$-deficient conditions in the autoclave that shifts the dirhodium catalyst equilibrium away from the hydroformylation dihydride catalyst,[1b] $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(et,ph\text{-}P4)]^{2+}$, to simple dirhodium carbonyl complexes that we believe are important for the aldehyde-water shift catalysis.

It is at this point under hydrogen depleted conditions that the aldehyde-water shift catalysis initiates. Average turnover frequencies (based on GC analysis) range from 1700 hr$^{-1}$ up to 2100 hr$^{-1}$. A representative reactant-product consumption-production plot is shown in Figure 2. We have not directly measured the $H_2$ being produced, but the stoichiometry of the reaction, number of turnovers, and high selectivity of the reaction leaves little doubt that $H_2$ is one of the products.
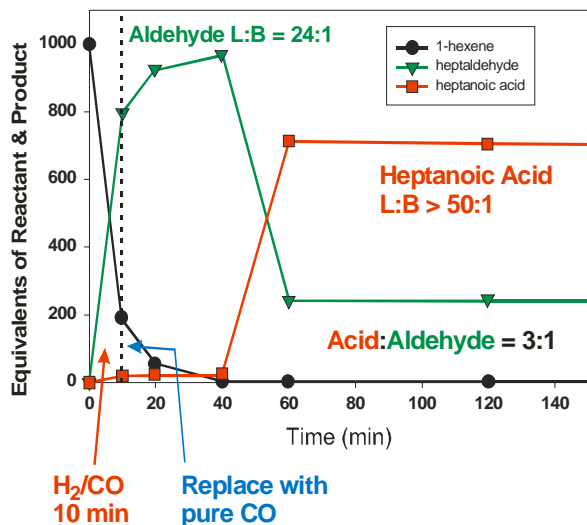


**Figure 2.** GC analysis of a tandem hydroformylation and aldehyde-water shift catalysis experiment.

The rapid production of $H_2$ leads to rapid inhibition of the aldehyde-water shift catalysis as seen after the 60 min mark in Figure 2. We typically get conversions of about 75% (750 turnovers), although we have seen one of our early runs with over 90%

conversion that had a relatively rapid accidental leak that purged hydrogen gas out of the autoclave.

We propose that the active catalyst species for the aldehyde-water shift catalysis is the dirhodium complex $[rac\text{-}Rh_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)](BF_4)_2$, **1** (see introduction for structural drawing). Under normal hydroformylation conditions with a 1:1 ratio of $H_2/CO$ no aldehyde-water shift catalysis is observed. We have established that the aldehyde-water shift catalysis is inhibited by the presence of too much $H_2$, although we have not established the precise amount. Interestingly, some hydrogen is necessary to form the CO-bridged species, **1**. We believe that hydrogen addition to the "open-mode" (non-CO bridged) isomer $[rac\text{-}Rh_2(CO)_4(et,ph\text{-}P4)]^{2+}$ makes a Rh dihydride complex that can far more readily close up to make the bridged CO hydroformylation catalyst complex $[rac\text{-}Rh_2H_2(\mu\text{-}CO)_2(et,ph\text{-}P4)]^{2+}$. Reductive elimination of $H_2$ from this species produces the bridged CO complex **1** critical for the aldehyde-water shift catalysis. **1** only exists in very low concentrations during hydroformylation catalysis when there is considerable $H_2$ present.

DFT quantum calculations on **1** indicate that the bridging CO ligands link and stabilize the lowest unoccupied molecular orbital (LUMO) making it a far better acceptor for activating the aldehyde for nucelophillic attack by water. The $\pi^*$ systems of both the terminal and bridging CO ligands form bonding interactions with the Rh $p_z$ orbitals. This lowers the energy of the LUMO of **1** by 0.8 eV relative to the open-mode, non-CO bridged isomer of **1**.

The direct conversion of aldehyde and water is more difficult because our autoclave systems are not designed as flow reactors. Nevertheless, we have successfully performed aldehyde-water shift catalysis by activating the catalyst precursor under $H_2/CO$, then using a constant purge of pure CO to react heptaldehyde and water (using 30% water in acetone as the solvent) to make heptanoic acid and $H_2$. The generality of the reaction was partially demonstrated by converting acetaldehyde and water to acetic acid and $H_2$. The volatility of the acetaldehyde, however, made this a considerably more difficult experiment and a slower purge rate had to be used to reduce the loss of acetaldehyde. Due to these experimental difficulties only 100 equivalents of acetaldehyde were converted. The ability to convert both heptaldehyde and acetaldehyde indicates that this reaction may work for aldehydes in general.

We are currently upgrading one of our autoclaves with a mass flow controller, condenser, and automated back-pressure regulator to setup a more sophisticated flow reactor system to study more volatile reactants such as acetaldehyde and especially formaldehyde.

**Conclusions**

Aldehyde-water shift catalysis is a new reaction for producing $H_2$ from water and aldehyde. The use of water both as an oxidizing agent and a source of the $H_2$ being produced is remarkable. We believe that bimetallic cooperativity in the proposed dirhodium catalyst $[rac\text{-}Rh_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)](BF_4)_2$, **1**, is playing an important role in helping to activate the aldehyde and to provide a low energy route for hydrogen production.

**References**
(1) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W. J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, *260*, 1784. (b) Matthews, R. C.; Howell, D. K.; Peng, W.-J.; Train, S. G.; Treleaven, W. D.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2253.
(2) Aubry, D. A.; Bridges, N. N.; Ezell, K.; Stanley, G. G. *J. Am. Chem. Soc.*, **2003***, 125*, 11180.